JOURNAL OF CATALYSIS **81,** 394–404 (1983)

Isomerization and Cracking of ^{13}C-Labeled Hexanes over H-Mordenite

I. Labeling of the Products and General Reaction Scheme

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Received October 5, 1981; revised September 10, 1982

The catalytic conversion of branched hexanes over H-mordenite at 170°C has been studied with a constant hydrocarbon pressure in a flow system. Under these conditions, isomers are desorbed first from the catalyst and cracked products (isobutane and isopentane exclusively) appear later on in the gas phase. Extrapolation of product distribution at zero conversion gives evidence for the occurrence of a direct interconversion between 3-methylpentane and 2,3-dimethylbutane and shows that 2-methylpentane is the only isomer yielding cracked fragments as primary products. The use of ^{13}C-labeled 3-methylpentanes demonstrates that isobutane, isopentane, and part of the hexanes result from the random association of ^{13}C and ^{12}C carbon atoms and that two types of isotopic isomer are formed. A detailed reaction scheme, involving the β-fission of a 2-methylpentenium-4 cation as initial step, is proposed to explain the formation of cracked products. It is suggested that sites of two different locations are involved in the reactions of hexanes on H-mordenite.

INTRODUCTION

In view of the high activity of zeolites in catalyzing hydrocarbon transformations, a great number of investigations on the mechanism of alkane isomerization and cracking over zeolite-based catalysts has been performed. Although the generation of an initial carbocation is still a subject of debate, results have been widely interpreted in terms of carbonium-ion chemistry involving intramolecular alkyl shifts, β-fissions, hydride transfers, condensation, and cyclization reactions (*1*). However, the determination of the individual reaction paths is generally complicated by the complexity of the reaction mixtures owing to numerous consecutive reactions at the temperatures required.

The objective of the present work was to study the isomerization and cracking of hexanes at low conversions and at moderate temperature in order to obtain insight into the primary rearrangements. ^{13}C tracer techniques have been used and, due to its remarkable activity (*2–4*), a synthetic mordenite has been chosen as catalyst.

EXPERIMENTAL

Materials

Alcohols. The synthesis of selectively ^{13}C-labeled 3-methylpentanols has been previously described (*5*). The same procedure, namely, the reaction of ethyl acetate with ethyl[2-^{13}C]iodide, was used to prepare 1,5-[$^{13}C_2$]3-methyl-3-pentanol.

The isotopic purity of the starting materials, ethyl-[2-^{13}C]iodide and ethyl-[1-^{13}C] acetate obtained from Merck Sharp and Dohme (Canada), was around 90%.

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0021-9517/83 $3.00

Hydrocarbons. The ^{13}C-labeled 3-methylpentanes used for the catalytic experiments were prepared as already described (*6, 7*) by catalytic dehydration and hydrogenation of the appropriate alcohol on a highly selective catalyst in a pulse flow system. The unlabeled 3-methylpentane, 2-methylpentane, and 2,3-dimethylbutane were Fluka puriss grade and were used without further purification.

Catalyst. The H-mordenite (Alite 180) used in this study was obtained from the Société Chimique de la Grande Paroisse. It was prepared by treating Na-mordenite (Alite 150) with HCl under mild conditions and had the following composition: Al_2O_3 = 11.9%, SiO_2 = 70.2%, Na_2O = 2.5%, $(NH_4)_2O < 0.1\%$, H_2O = 15.1%, Si/Al = 5. It was activated at 550°C in a stream of dry air for 2 hr and then stored at room temperature.

Apparatus and Procedures

The catalytic reactions were carried out in an all-glass grease-free flow apparatus. Reactants were introduced at constant pressure in a flow of purified hydrogen (1 atm, 40 to 60 ml/min) in the reactor where the catalytic bed (200 mg), isothermal, operated at the reaction temperature. Two calibrated katharometers were inserted in the flow line before and after the reactor in order to detect possible diffusional effects and/or to estimate the amounts of materials left on the catalyst (*8*).

Before each run the fresh catalyst was heated for 2 hr under hydrogen flow at the reaction temperature (170°C). For product distribution determinations, part of the effluent gas was deviated through a 20 lusec[3] glass leak into a 250-ml reservoir and analyzed by GLC at the end of a catalytic run. In some experiments 5-ml samples were collected directly from the flow line through a rubber septum at different stages of the reaction and analyzed separately.

For ^{13}C experiments, products were collected in liquid nitrogen cooled traps and fractionated by preparative GLC.

GLC Analysis

A 5 m × ⅛ in. column of DC-200/firebrick operating at 50°C and a flame ionization detector were used for the analysis of the various hydrocarbons. For the preparative separations a 5 m × ¼ in. column of SE 30/firebrick was used at room temperature.

Mass Spectrometric Analysis

The mass spectra were recorded on a Varian Mat CH7 apparatus using 70 V electrons to ionize the molecules. Mass spectra of isobutane and isopentane were obtained by using the direct inlet system and a high resolution (ca. 3000) to resolve the multiplets at masses m/e = 44,28.

The mixtures of C_6 hydrocarbons were analyzed by using a mass spectrometer–gas chromatograph coupling device. The procedures and experimental conditions of the analysis have been described elsewhere (*7, 9*).

Calculations. The recorded mass spectra were corrected for naturally occurring isotopes and C–H fragmentation in order to obtain the percentages of the various parent ions $^{13}C_a{}^{12}C_{n-a}H_{2n+2}{}^{\oplus}$ and main fragments $^{13}C_a{}^{12}C_{m-a}H_{2m+1}{}^{\oplus}$. The location of the carbon 13 in the monolabeled methylpentanes and 2,3-dimethylbutanes has already been discussed (*5, 7, 10*). In some experiments complete scrambling of the reaction products occurred. The total spectra of these molecules (parent and fragment ions) were calculated from the fragmentation patterns of the corresponding nonlabeled molecules and the binomial expansion. The theoretical and experimental spectra were then compared by calculating the mean square deviation (Δ) between the observed and calculated ^{13}C distributions.

$$\Delta = \sum_{i=0}^{i=n} ({}^{13}C_{i\,\mathrm{obs.}} - {}^{13}C_{i\,\mathrm{calc.}})^2$$

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[3] lusec (from litre, μ, and second) = 1.33×10^{-4} Pa $m^3\ s^{-1}$.

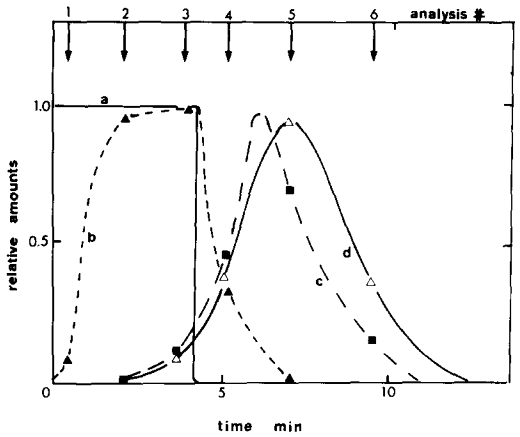


FIG. 1. Relative amounts of products desorbed from H-mordenite at 170°C vs time: (a) 3-methylpentane-starting hydrocarbon; (b) isomers (2,3DMB, 2MP); (c) isopentane; (d) isobutane.

RESULTS

Reactions of Nonlabeled hexanes: Product Distributions

The catalytic behavior of H-mordenite in the reactions of branched hexanes at low conversion was investigated at 170°C. Typically 3 μl of reactant was introduced in the flow line at a constant partial pressure of 5 Torr (1 Torr = 133 Pa). Under these conditions, the signals given by the two calibrated katharometers placed before and after the catalytic bed remained rectangular and had the same area showing that, in contrast to what was observed with olefins (*8*), no appreciable amounts of material were left on the surface during the reaction.

Analysis of the exit gas from the reactor revealed that the product distribution changed continuously with time. This is illustrated in Fig. 1 where the relative amounts of products and reactant (here 3-methylpentane) present in the gas phase are plotted versus time for an experiment in which six analyses were made at different stages of the reaction as represented by arrows in the figure. During the first minutes of the run (analyses 1 to 3), while 3-methylpentane (3MP) was contacted with the catalyst, the major reaction products detected were isomers. Their formation increased sharply to reach a steady value and then dropped rapidly at the end of the 3MP pulse. Cracked products (mainly isobutane and isopentane) appeared in the gas phase in significant amounts only after the drop of the reactant signal (Analysis 4). Note that isomers were still detected at this point. The changes with time of the concentrations of isobutane and isopentane followed Gaussian type curves whose maxima were reached with an important delay with respect to the end of the 3MP pulse and conversely to the appearance of the isomers. Such an effect of "delayed desorption" of the products, which was independent of the starting hydrocarbon, suggests that cracking and isomerization occur on different sites of the zeolite.

More precise analyses of the reaction products recovered by using the leak-reservoir system are given in Tables 1, 2, and 3 for the reactions of 3-methylpentane, 2-methylpentane (2MP), and 2,3-dimethylbutane (2,3DMB), respectively. Collecting times were determined in order to avoid erroneous conclusions due to the "delayed desorption" effect. The variations in conversion levels were achieved by varying the hydrogen flow rate.

The main products formed were isobutane and isopentane and, among the isomers, branched hexanes, *n*-Hexane (*n*H) was observed only at higher conversions.

TABLE 1

Reaction of 3-Methylpentane at 170°C: Product Distribution (Mol%)

Run number	Conversion (%)	C_3	iC_4	iC_5	2,3DMB	2MP	*n*H
1	0.2	—	3.8	—	10.3	85.9	—
2	0.4	—	5.8	—	11.6	82.6	—
3	1	0.2	5.9	—	12.3	78.7	—
4	1.4	0.4	9.6	4.7	11.9	73.4	—
5	3.5	0.5	28.7	13	8.2	49.2	—
6	4.8	1.0	32.3	13.9	7.6	45.1	—
7	7.4	1.2	33.8	13.5	7.5	43.6	0.5
8	7.9	1.3	34.8	13.7	7.3	42.6	0.3
9	8.5	1.8	36.7	13.9	6.9	40.2	0.5
10	8.9	0.6	38.6	14.4	6.9	39.2	0.3

TABLE 2

Reaction of 2-Methylpentane at 170°C: Product Distribution (Mol%)

Run number	Conversion (%)	C_3	iC_4	iC_5	2,3DMB	3MP	nH
11	1.1	2.6	36.7	12.5	8.0	40.2	—
12	2.0	1.1	40.8	15	8.9	34.2	—
13	2.1	2.3	36.4	14.4	9.2	37.7	—
14	3.1	0.6	38.3	14.9	11.1	35.1	—
15	4.4	0.1	38.7	15.3	11.7	33.1	—
16	5.5	1.3	35.9	14	16	32.8	—
17	11.6	0.1	37.4	17.4	19.8	25.1	0.3

TABLE 3

Reaction of 2,3-Dimethylbutane at 170°C: Product Distribution (Mol%)

Run number	Conversion (%)	C_3	iC_4	iC_5	2MP	3MP	nH
18	1	—	15	10.1	42.2	32.7	—
19	2.4	—	32.6	17.5	27.9	22.2	—
20	4.6	—	42.9	19.5	19.5	18	—
21	5.5	1.7	50.7	15.5	13.6	12.9	—
22	6.7	—	50.3	15.8	18.5	14.7	0.4

Light products (exclusively propane) represented always less than 3% of the total reaction products. In some experiments olefins, mostly isobutene and isopentene, were detected but at a nonquantifiable level. 2,2-Dimethylbutane (2,2DMB) was looked for and could not be detected. These distributions show that, under the experimental conditions, the only molecules desorbed are the ones derived from tertiary carbocations and that intermolecular hydride transfers are of great importance.

Extrapolation of product distribution at zero conversion has been used to identify primary and secondary reaction products (*11*).

As shown by the positive values of the selectivities at zero conversion all the products (cracked products and isomers) were primary products from 2-methylpentane (Fig. 2). In contrast, 3MP and 2,3DMB yielded only isomers (2MP and 2,3DMB and 2MP and 3MP, respectively) as primary products (Figs. 3 and 4).

The initial ratios ρ_1 = 3MP/2,3DMB in the reaction of 2MP, ρ_2 = 2MP/2,3DMB in the reaction of 3MP, and ρ_3 = 2MP/3MP in the reaction of 2,3DMB are equal to 4.8, 7.4, and 1.5, respectively, and show moreover that in the interconversion of tertiary hexyl cations, the nonbranching rearrangements (2MP $\rightleftarrows$ 3MP) are only slightly faster than the branching ones (MP $\rightleftarrows$ 2,3DMB) and that 2MP and 3MP are formed with comparable rates from 2,3DMB. Note that the ρ_i values obtained are consistent with first order kinetics (see Appendix).

Reactions of Labeled 3-Methylpentanes

Cracked products. The cracking process has been studied with a doubly labeled molecule: the [1,5-$^{13}C_2$]3-methylpentane. This

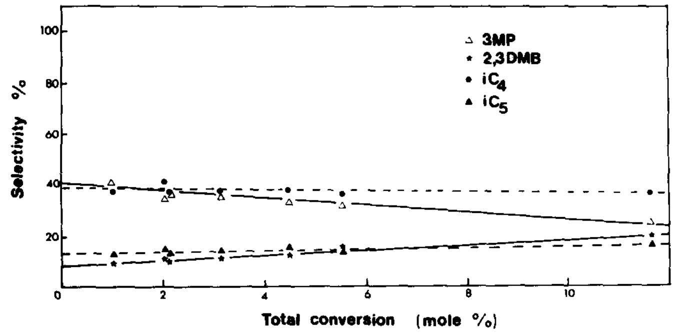


FIG. 2. Reaction of 2-methylpentane at 170°C. Product selectivity versus total conversion.

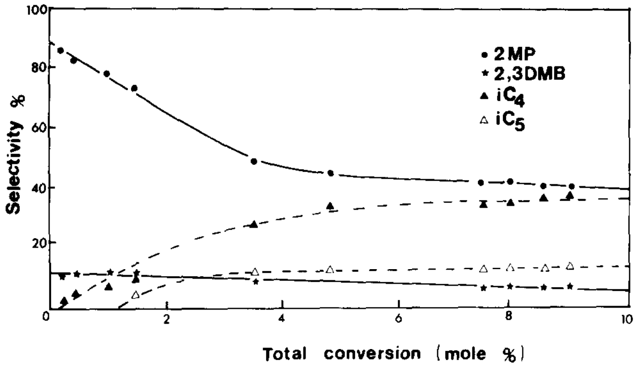
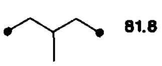
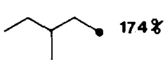
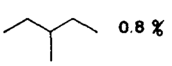


FIG. 3. Reaction of 3-methylpentane at 170°C. Product selectivity versus total conversion.

molecule was synthesized by using the procedure described in the experimental section which resulted in the following labeling determined by mass spectrometry (*10*):







and a ^{13}C enrichment of 30.2% per carbon atom.

The mass spectrometric analyses of isobutane and isopentane formed in a reaction at 7.9% conversion (run 8, Table 1) are listed in Table 4.

The ^{13}C distribution of the molecular ions and of the demethylated and deethylated fragments corresponded exactly to a statistical binomial distribution where all carbon atoms (^{13}C and ^{12}C) were randomized. In the same experiment, analyses of 2-methylpentane and 2,3-dimethylbutane had also been made. The data are reported in Table 5. For both isomers the ^{13}C distribution of the parent ions was better explained by combining linearly two distributions: one associated with a unimolecular isomerization process in which the isotopic content of the starting hydrocarbon is preserved: distribution I; the other corresponding to a complete randomization of all carbon atoms as observed for the cracked products: distribution C.

The low values of the mean square deviations (MDS = Δ) between the observed and calculated distributions obtained by such a treatment would indicate that the contribution to the cracking process (associated to distribution C) in the formation of the isomers would be 4% for 2-methylpentane and up to 9% for 2,3-dimethylbutane. Lastly, the ^{13}C enrichment of all products was the same as that of the reactant 3-methylpentane.

Isomers. More information on the labeling of the isomers formed according to the unimolecular process (distribution I) was obtained by reacting monolabeled [3-^{13}C]3-

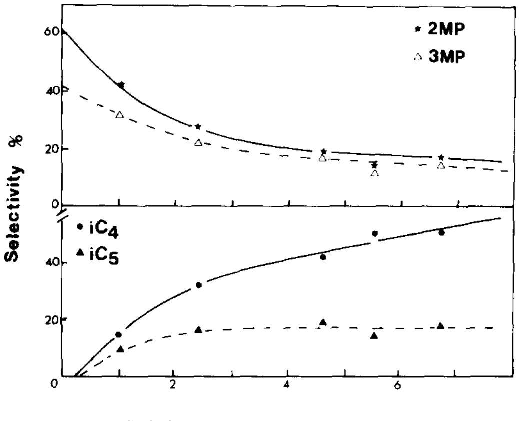


FIG. 4. Reaction of 2,3-dimethylbutane at 170°C. Product selectivity versus total conversion.

TABLE 4

Cracking of [1,5-$^{13}C_2$]3-Methylpentane Calculated and observed Mass spectra: Isobutane and Isopentane

Ions	Isobutane			Isopentane		
	$^{13}C_i$	Observed	Calculated (random)	$^{13}C_i$	Observed	Calculated (random)
Parent	$^{13}C_4$	0.6	0.7	$^{13}C_4$	0.2	0.2
	$^{13}C_3$	6.0	7.1	$^{13}C_3$	1.9	2.7
	$^{13}C_2$	27.0	25.8	$^{13}C_2$	11.1	12.8
	$^{13}C_1$	43.2	41.4	$^{13}C_1$	33.6	30.5
	$^{13}C_0$	23.3	24.9	$^{13}C_0$	16.0	17.4
		$\Delta = 7.3$			$\Delta = 15.1$	
Demethylated				$^{13}C_4$	0.3	0.8
	$^{13}C_3$	2.5	1.9	$^{13}C_3$	5.8	7.2
	$^{13}C_2$	18.2	17.7	$^{13}C_2$	26.3	25.9
	$^{13}C_1$	43.9	45.7	$^{13}C_1$	42.9	41.3
	$^{13}C_0$	35.4	34.7	$^{13}C_0$	24.6	24.7
		$\Delta = 4.2$			$\Delta = 5.0$	
Demethylated				$^{13}C_3$	2.7	2.6
				$^{13}C_2$	18.8	18.4
				$^{13}C_1$	45.0	44.0
				$^{13}C_0$	33.5	35.0
					$\Delta = 3.4$	
% ^{13}C		29.4			29.5	

methylpentane. Reaction products were collected in two fractions. The first fraction was obtained during the first 4 mins, while [3-^{13}C]3-methylpentane was fed onto the catalyst, and the second during the following 10 min, just after the drop of the rectangular reactant signal (see Fig. 1).

Results are given in Table 6. As in the case of the experiment made from [1,5-$^{13}C_2$]3-methylpentane, multilabeled species were detected in all hydrocarbons. Again the observed distributions could be fairly well reproduced by combining linearly a type I (unimolecular process) and a type C

TABLE 5

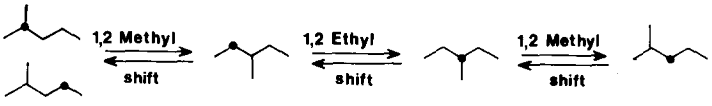
Isomerization of [1,5-$^{13}C_2$]3-Methylpentane Calculated and Observed Mass Spectra of 2-Methylpentane and 2,3-Dimethylbutane

$^{13}C_i$	Theoretical[a]		2-Methylpentane		2,3-Dimethylbutane	
	Initial dist. I	Randomized dist. C	Observed	0.96I + 0.04C	Observed	0.91I + 0.09C
$^{13}C_0$	0.8	11.7	1.4	1.2	1.5	1.8
$^{13}C_1$	17.4	30.2	17.9	17.9	18.7	18.5
$^{13}C_2$	81.8	32.4	79.8	79.8	77.2	77.4
$^{13}C_3$	—	18.6	0.9	0.7	1.9	1.7
$^{13}C_4$	—	6.0	—	0.2	0.7	0.6
				$\Delta = 0.1$		$\Delta = 0.2$
% ^{13}C	30.2		30.0		30.3	

[a] See text for meaning of I and C.

(complete randomization of all carbon atoms) distribution. The coefficients introduced into the linear combinations showed that the contribution of the mechanism associated with distribution C is much more important in the products collected in fraction II than in those recovered in fraction I. For example, in fraction II up to 10% of the 3-methylpentanes was formed according to this latter mechanism whereas in the first fraction only monolabeled 3MP (with a type I distribution) was detected.

After correction of the observed spectra for the contribution of the type C distribution, the distribution of the monolabeled species was obtained. Among the methylpentanes, besides the isomers which could result from rearrangements involving classical alkyl shifts (Scheme 1):

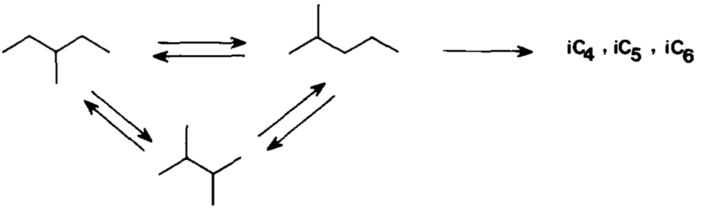


SCHEME 1.

"abnormal" species, namely, [1-^{13}C]2-methylpentane and 3-methyl[^{13}C]pentane, were also observed. The respective percentages of these "abnormal" species in each fraction showed that the monolabeled methylpentanes of the second fraction (corresponding to the "delayed desorbed" products) underwent deeper rearrangements than those formed in the first stage of the reaction. (Note, however, that the distribution of the species in the second fraction is still far from that associated with a complete scrambling of the label.) In contrast, no change in the labeling of 2,3-dimethylbutane was noted. In both fractions 40% of the label was found in position 1 and 60% in position 2.

DISCUSSION

The experimental data described in the preceding section show that the acid-catalyzed rearrangements of branched hexanes over H-mordenite at 170°C proceed, at low conversion, via the overall reaction scheme (Scheme 2):



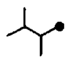
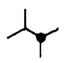
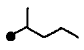
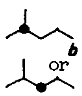
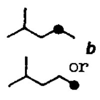
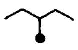
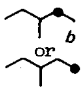
SCHEME 2.

The three main features of this scheme are: (i) The total absence among the isomers of *n*-hexane and 2,2-dimethylbutane, which shows that, under our conditions, the rearrangements which could lead to the formation of these hydrocarbons have negligible reaction rates when compared to the interconversions of the tertiary hexyl cations. (ii) The direct transformation between 3-methylpentane and 2,3-dimethylbutane. (iii) The occurrence of isomerization reactions not accompanied initially by cracking, which shows that the key step of the cracking process is not the generation of the tertiary hexyl cations.

Moreover, from the specific labeling of

TABLE 6

Isomerization of [3-^{13}C]3-Methylpentane: Labeling of the C_6 Products

Hydrocarbon	2,3-Dimethylbutane				2-Methylpentane					3-Methylpentane				
	Dist. C%[a]	Monolabeled species		%[c]	Dist. C%[a]	Monolabeled species			%[c]	Dist. C%[a]	Monolabeled species			%[c]
														
Fraction I[d]	6	39.1	60.9	2.8	7	0.2	71.4	28.4	12.2	0	0	16.7	83.3	85
Fraction II[d]	20	41.7	58.3	5	15	11.8	56.1	32.1	25	10	1.7	33.9	64.4	70
Scrambled[e] distribution		66.6	33.3			33.3	33.3	33.3			16.6	66.6	16.6	

[a] Percentages of molecules with a randomized distribution of the ^{13}C.

[b] Species not distinguishable by mass spectrometry.

[c] Percentages among hexanes.

[d] See text.

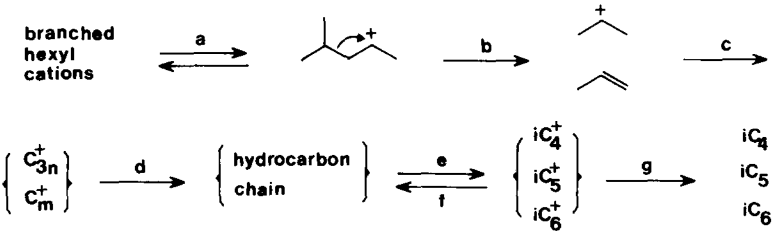
[e] Equal distribution of the label on all carbons of the hexane.

the reaction products obtained in the ^{13}C tracer studies, it is apparent that the interconversions of branched hexanes (left-hand part of the scheme) and the formation of cracked products (iC_4, iC_5, and part of the iC_6) may be formally considered as two distinct processes.

The complexity of the ^{13}C labeling of the cracked products formed from saturated hydrocarbons over acidic zeolites has already been reported by Bolton *et al.* (*12*). In the reaction of *n*-[3-^{13}C]pentane on ammonium-exchanged Y zeolite these workers showed that the ^{13}C distribution of the cracked products was near random and it was suggested that these products were formed through the random breakdown of adsorbed polymer material. In a more recent paper (*13*) Fajula and Gault reported that the initial products formed in the reaction of [2-^{13}C]methylpropene on H-mordenite at 170°C were isobutane and isopentane with a completely randomized distribution of the ^{12}C and ^{13}C carbon atoms. In this latter work a detailed reaction scheme is proposed where the formation of tertiobutyl and tertioamyl cations is explained by a continuous breakage and reformation of polymeric chains attached to the zeolite framework. Hydride transfers between the chains and the cations lead to the desorption of saturated hydrocarbons and the formation of hydrogen-poor strongly adsorbed residues. Furthermore the ^{13}C distributions are accounted for by a succession of collisions between the free cations and the adsorbed hydrocarbon chain and it is demonstrated that only four adsorption–desorption steps are enough to reach the statistical distribution.

The similarities between the product and ^{13}C distributions observed in the present work and the ones described by Bolton *et al.* and Fajula and Gault strongly argue for the participation of a similar type of mechanism in all three reactions. Moreover, this mechanism involves the formation of polymeric hydrocarbon chain intermediates whose structures are independent of the starting material.

The question is thus to know how such a polymeric intermediate can be generated from a hexane molecule. Several experiments (*14–16*) clearly demonstrate the effectiveness of trace olefins in initiating cracking reactions of saturated hydrocarbons. This can be understood by the easiness of olefins in forming heavier products by classical cationic polymerization. The fact that 2-methylpentane, which is the smallest structure allowing generation of an olefin by a direct *β*-fission without formation of an unstable primary cation, is the single isomer yielding cracked fragments as primary products suggests therefore the participation of propylene and propylium ion in the initiation step. The detailed pathway for the cracking of hexanes over H-mordenite could be thus represented by the following scheme (Scheme 3):



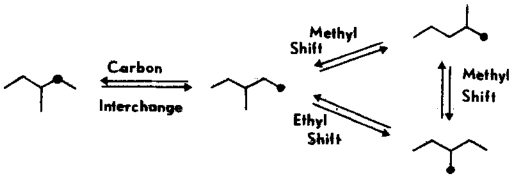
SCHEME 3.

with as individual steps: a, isomerization of the hexyl cation; b, *β*-fission of the 2-methylpentenium ions; c, polymerization, alkylation; d, skeletal rearrangement of the oligomer leading to a partial scrambling of the ^{13}C; e and f, depolymerization–polymerization steps leading to a complete label scrambling (distribution C); g, desorption of the scrambled cations by hydride transfer.

The absence of significant amounts of propane among the gaseous products is explained by rapid alkylation reactions between the highly reactive secondary propylium ion and partially dehydrogenated fragments. It is worth mentioning that in the reaction of propylene on H-mordenite at 170°C (*13*) large quantities of isobutane and isopentane are formed, whereas propane is not detected.

Let us now consider the hexane products. From the data in Fig. 1 and Table 6 two regimes can be distinguished. In the first stages of the reaction, the main products are monolabeled methylpentanes and 2,3-dimethylbutanes whose production can be explained by considering classical intramolecular nonbranching and branching rearrangements (*1, 17*) of the hexyl cations. Molecules with a random association of six carbon atoms (distribution C) are present, but in small quantities. These latter hydrocarbons do not result from a true isomerization process and are obviously formed according to the mechanism described in Scheme 3.

At the end of the run, in the so-called delayed products, "normal" isomers (namely methylpentanes labeled in positions 2, 3, and 4 and 2,3-dimethylbutanes) are still formed. However, one notices a large increase in the amounts of totally randomized molecules and the appearance of a new class of monolabeled isomers such as [1-^{13}C]2-methylpentane and 3-methyl[^{13}C]pentane. The formation of these isomers necessitates, besides simple alkyl shifts, the occurrence of an interchange reaction between internal and external carbon atoms (Scheme 4).



SCHEME 4.

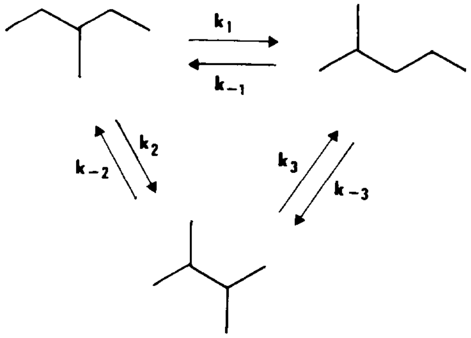
The striking difference between the distribution and the labeling of the products collected at the beginning and at the end of the run originates, we believe, from two different locations of the active sites. Moreover, it has been proposed (*13*) that the polymerization–depolymerization reaction, which accounts well for the production of hydrocarbons with a statistical distribution of the label, were initiated by acid centers situated inside the mordenite channels.

It is therefore tempting to establish a correlation between the various reaction processes and the location of the acid sites. We therefore propose that the alkyl shifts and interconversions between the methylpentanes and 2,3-dimethylbutane (leading to the "normal" isomers) could take place on sites of any location. Due to their greater accessibility one may expect, however, that the more external ones would be the more efficient in forming these products. In contrast, the molecules with a random distribution of the ^{13}C and ^{12}C carbon atoms and the isomers resulting from an internal–external carbon interchange would be formed essentially inside the zeolite channels. Pore diffusion and/or the existence of strong interactions between the organic cations and the rigid counteranions would then be responsible for their long residence time on the catalyst.

A complete description of all the rearrangements in terms of unambiguous structures of the ionic intermediates is difficult at this time. It can be speculated that the reactivity of the hexyl cations will be strongly affected by some subtle differences in the structure of the adsorbed species on the surface. A careful analysis of the isotopic varieties obtained from molecules labeled with ^{13}C in various positions is highly desirable and will be presented in Part II (*18*).

APPENDIX

Assuming first-order kinetics and considering the ρ_i ratios we obtain:



$$\rho_1 = \frac{k_{-1}}{k_{-3}} = 4.8$$

$$\rho_2 = \frac{k_1}{k_2} = 7.4$$

$$\rho_3 = \frac{k_3}{k_{-2}} = 1.5$$

$$\frac{k_3}{k_{-2}} = \frac{k_1}{k_2}\left(\frac{k_{-1}}{k_{-3}}\right)^{-1} \cdot \frac{k_{-1}}{k_1} \cdot \frac{k_2}{k_{-2}} \cdot \frac{k_3}{k_{-3}}$$
$$= 7.4 \cdot \frac{1}{4.8} \cdot \frac{3\mathrm{MP_e}}{2\mathrm{MP_e}} \cdot \frac{2{,}3\mathrm{DMB_e}}{3\mathrm{MP_e}} \cdot \frac{2\mathrm{MP_e}}{2{,}3\mathrm{DMB_e}}$$

where e denotes thermodynamic equilibrium, = 7.4 · 1/4.8 = 1.54 in good agreement with the obtained value of 1.5.

ACKNOWLEDGMENTS

The authors express their profound gratitude to the late Professor François G. Gault who initiated and encouraged this investigation and they also thank the referees for their constructive remarks.

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